Biomaterial gelatin film based crossbar structure resistive switching devices

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Abstract—Crossbar structural resistive switching devices (memristors) are fabricated using biomaterial gelatin film as the dielectric layer. The performance of the devices and the effects of gelatin film thickness and baking temperature are investigated. Results show that the optimal gelatin film thickness for the memristors is ~80 nm and baking temperature ~105 ^{o}C. The optimized memristors show a bipolar resistive switching behavior with the resistance ratio between the high resistance state and low resistance state over 10^2, the retention time over 10^6 sec without any obvious deterioration, and excellent stability and reliability, demonstrating its good potential for applications. A conductive atomic force microscopy is used to study the conductivity of the gelatin films under various biases, and the results indicate that the conductive filaments are responsible for the resistive switching behavior of the gelatin-based memristors.

Keywords—memristors; gelatin dielectric; cross-bar array device; bioelectronics

I. INTRODUCTION

Memristors are a new type of memory devices with a resistive switching behavior, and data information can be stored in the devices efficiently at high speed through the change of resistive values of the devices. The device working mechanisms and structures have been extensively investigated, and their applications have been widely exploited. Owing to the attractive characteristics of simple structures, low power consumption, high read-write speeds and easy integration with other electronics, memristors have demonstrated the great potential to be the next

generation of memory devices[1, 2]. Although various dielectric materials such as oxides, polymers have been investigated to fabricate memristors, transition metal oxides such as TiO_2, ZnO[3, 4], NiO[5] have been the dominant dielectric materials with the Metal-Oxide-Metal (MOM) [6, 7] sandwich structure as they can be simply integrated with current Complementary metal-oxide- semiconductor (CMOS) technology. Memristor array using neural network training were also developed to build a cognitive system [7, 8]. On the other hand, with the ever-increasing concerns for healthcare, medicine and environments, the development of biocompatible, biodegradable and environmentally friendly electronics, the so-called green electronics, has become a pressing issue and a hot research topic for both academia and industry[9, 10]. Owing to the merits of wide availability, flexibility, printable capability, and easy process and low cost[11, 12], many types of biomaterials, such as DNA[13], protein[10, 14, 15], nucleobases[16], paper[17, 18] and gelatin[19, 20], have been explored for the fabrication of various green electronic devices, as well as memristors with the simple Metal-Insulator-Metal (MIM) sandwich structure[20]. We have also demonstrated a type of biocompatible transitional memristors using soluble albumen dielectric layer and tungsten (W) and magnesium (Mg) as the electrodes [13], and showed their potential for transitional implants or medical application.

Gelatin is a biomaterial obtained from animal skins, bones etc, and it has a quasi-reversible water dissolving property[21]. Recent work has shown that gelatin could be a suitable dielectric material for the fabrication of memristors with good properties[19, 20], but very limited work has been done for in-depth understanding of the device properties and process influence, and more work is needed before its application. The working mechanism of the devices is still not clear, and the repeatability, reliability and stability of the devices are yet to be investigated.

This paper reports the fabrication and characterization of a 4×4 crossbar structural memristors using gelatin as the dielectric layer. The effects of gelatin film thickness and baking temperature on the device performance are investigated. Under the optimal conditions, the gelatin-based memristors exhibit excellent bipolar resistive switching behavior, and long retention property and brilliant stability, demonstrating its potential for promising applications. A conductive atomic force microscopy (C-AFM) is used to study the working mechanism of the devices.

II. EXPERIMENTAL DETAILS

Fig. 1(a) shows the three dimensional (3D) schematic drawing of the 4 × 4 crossbar memristor array for this research. The memristors consist of tungsten bottom electrodes, a gelatin dielectric layer and magnesium top electrodes, on a Si substrate with a 300 nm thickness thermally-grown oxide. The Si-substrate was used as a support only for easy fabrication. The width and length of the crossbar are 100 μm and 1900 μm, respectively, while the dimensions of the pads are 200 μm × 200 μm. The fabrication process is as follows**:** The tungsten electrodes were patterned and formed by photolithography and lift-off process, using direct current (DC) magnetron sputtering method at a base pressure of 3×10^{-3} Pa, a sputtering power of 290 W with a deposition rate of ~20 nm/min. After removing the photoresist and cleaning, a gelatin layer was spun on the substrate with the W-electrodes, and then baked on a hotplate. The top Mg electrodes were fabricated by DC magnetron sputtering via a metal mask, at a base pressure of 3×10^{-3} Pa and a sputtering power of 230 W, with a deposition rate of ~20 nm/min. The thickness of both the tungsten and magnesium electrodes is ~80 nm.

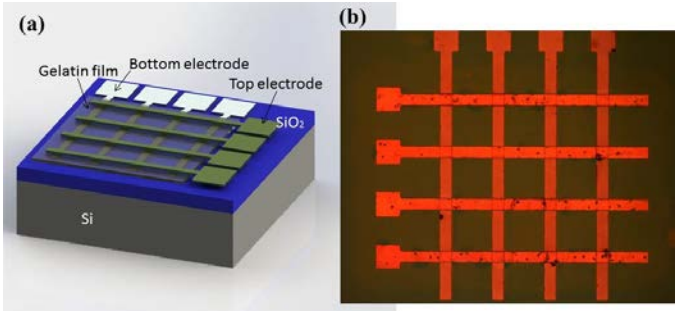

Figure 1. (a) A 3D schematic drawing of the crossbar memristor device with 16 bipolar resistive switching cells, and (b) a microscope image of the fabricated devices. The width and length of the crossbar are 100 μm and 1900 μm respectively.

The gelatin solution was prepared as follows: 1.5 g gelatin powder (Biosharp, China) was dissolved into 60 ml deionized (DI) water at room temperature for 30 min until it was fully dissolved, and then the solution was stirred continuously at an elevated temperature of 50 ^{o}C for one hour to make it uniform. The cooled-down gelatin solution was spun on the substrate with patterned bottom electrodes at 4000 rpm for 40 sec which resulted in a thickness of ~80 nm. The wafer was baked for 12 min at different temperatures. Since the gelatin film thickness and baking temperature were found to influence the performance of the memristor devices significantly, their

effects on the devices were investigated in detail. The thickness of gelatin layer was varied from 30 nm to 160 nm, and the baking temperature was from 60 to 160 ^{o}C. Fig. 1(b) shows a microscopic image of the fabricated memristor device with 16 resistive switching cells.

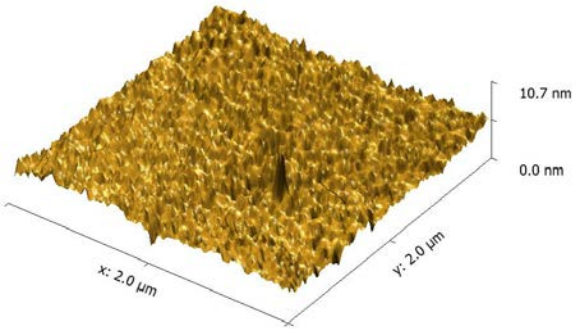

Figure 2. A typical AFM topological image of the surface of the gelatin film used in this work (80 nm thickness, 105 ºC baking temperature), showing a RMS roughness of ~4.1 nm.

The resistive switching cells were characterized by the semiconductor parameters analyzer (B1500, Agilent) in cleanroom, on a probe station directly. Conductive atomic force microscopy (AIST-NT) was used to characterize the topology and the conductivity of the gelatin film at room temperature. Fig. 2 is a typical AFM topological image of the gelatin film with a scan area of 2 μm x 2 μm. It shows a typical RMS (Root mean square) surface roughness of about 4.1 nm for this film. The RMS surface roughness for 30 and 160 nm films are roughly 2.5 and 6.2 nm respectively, increasing with the film thickness slightly.

III. RESULTS AND DISCUSSION

A. Device characteristics

Fig. 3(a) shows the typical current-voltage (I-V) curve of a gelatin-based memristor device. When the top electrode is positively biased with the bottom electrode grounded, the current increases gradually with the increase of applied voltage. The fabricated devices need an initial forming process at high voltages, typically 6-8 V as shown in the inset, to obtain a bipolar resistive switching behavior and the set and reset voltages of the devices are then stabilized. Once formed, the device is at the low resistance state (LRS). When the voltage increases and approaches 4.0 V, an abrupt increase in current can be observed, corresponding to the “set” process for the resistive switching devices. At this moment, the device changes from the high resistance state (HRS) to the low resistance state, i.e. the device is switched from the ‘OFF’ state to the ‘ON’ state. A preset

current compliance of 2×10^{-4} A was applied to protect the memristors. The resistance ratio between the HRS and LRS at 0.1 V is up to 10^4, better than those of other biomaterials based memristors[22, 23], and even comparable to those of metal oxides based devices[16], demonstrating the excellent resistive switching behavior of the Mg/gelatin/W memristors. To "reset" the device to the HRS, a negative voltage is applied to the top electrode with the bottom electrode grounded. The reverse current increases with the negative bias, and at ~-4.5 V, the current falls dramatically by about four orders of magnitude. The device returns to the HRS, i.e. the device has been reset.

For better understanding of the working mechanism of the resistive switching process, the I-V curves of Fig. 3(a) are re-plotted in a double logarithmic plot as shown in Fig. 3(b). It is clear that both the forward and reverse biased I-V curves at low voltage regions can be linearly fitted with the positive and negative voltage, respectively. For the LRS as shown in Fig. 3(b), the slope of the log(I)-log(V) curves is close to the unity, indicating that the transportation of electrons is dominated by the Ohm's law for both the positive and negative voltage sweeps. For the HRS, the slope of the log(I)-log(V) curves are approximately the unity at the low voltage region, and is similarly dominated by the Ohm's law. In the high voltage region (2~4 V), the slope is ~2 and becomes larger with further increase in bias, which corresponds to the trap-controlled filling process[14, 24], similar to those observed from the oxide based memristors.

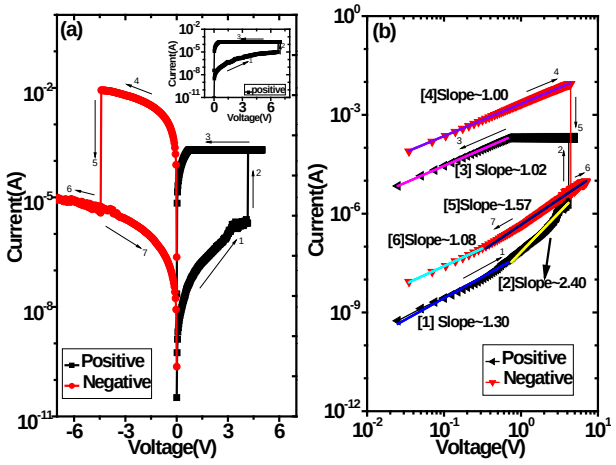

Figure 3. (a) A typical I-V curve of the memristors fabricated, the inset is the forming process of the device, and (b) I–V curves in a double logarithmic plot for the positive and negative voltage sweepings. The lines are the fittings. The arrows indicate the sweeping direction of the voltages.

Endurance test was carried out to investigate the stability of the memristors. A cyclic voltage was applied to the device to change it from "OFF->set->ON->reset" for over 80 times. As shown in Fig. 4(a) with the data measured at a bias of 0.1V, the resistance of the memristor at the LRS is within a relatively stable range from 1000 to 3000 Ω, while the HRS resistance fluctuates randomly within the range between 10^5 and 10^7 Ω. Although the HRS resistance varies largely, the typical resistance ratio between the HRS to LRS is more than 10^2, sufficiently high for application without causing circuit problem. It is worthy to point out that memristors with polymer or biomaterial dielectric layers all showed a large dispersion of the resistance at the HRS. Fig. 4(b) illustrates the result of retention test on a device for over 10^6 sec, with the data taken at a bias of 0.1 V. The device maintains stable resistance values of the HRS and LRS, with an almost constant resistance ratio even after operated for two weeks, demonstrating its brilliant and reliable performance of the devices fabricated.

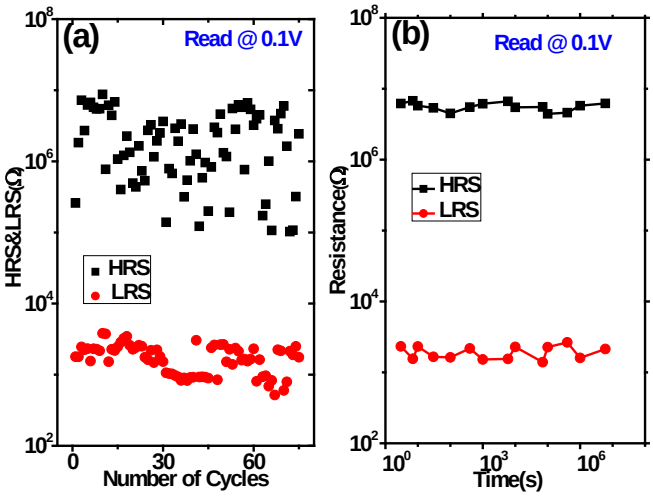

Figure 4. (a) Endurance test for a memristor cell from the HRS to LRS for 80 cyclic tests with the resistances taken at a bias of 0.1 V, and (b) retention test of the HRS and LRS with the resistance measured at a bias of 0.1 V for up to 10^6 sec, showing excellent stability of the devices.

B. Structure and process effects

Memristors with different gelatin film thicknesses and baking temperatures were prepared to study their effects on the properties of the devices. Fig. 5(a) shows the I-V characteristics for the devices with varying gelatin film thickness. It is clear that the gelatin thickness has a significant effect on the "set" and "reset" voltages of the devices. The set voltage is approximately ~0.7 V, ~4

V and ~7.2V for the devices with a gelatin film of 30 nm, 80 nm and 160 nm, respectively, increasing rapidly with the film thickness. The same trend was observed for the reset voltages of the devices as well. The corresponding average set electric field for these film thicknesses is 2.3×10^7, 5×10^7 and 4.5×10^7 V/m, respectively. The set electric fields for the devices with 80 and 160 nm gelatin film are comparable, while that for 30 nm gelatin layer has an average set electric field half of others, indicating "the conductive filaments" can be formed at lower electric fields for devices with thinner gelatin films. This is probably related to the roughness of the gelatin layer and the inter-diffusion of metal elements from the electrodes, resulting in a reduced effective dielectric layer, which is much more significant for the thinner gelatin devices. On the other hand, the resistance value for the HRS seems not to change much when the thickness varies, whereas the LRS resistance changes significantly from 2×10^3 to 1.9×10^4 Ω. The phenomenon of the increase of set voltage with the film thickness can be explained by the conductive filament model, when the film thickness increases, the conductive filament length increases, so that it needs higher voltage to set the device, and the same applies for the reset process.

Fig. 5(b) shows the ON/OFF resistance ratio taken at 0.1 V. For the device with an 80 nm gelatin layer, it exhibits a maximum ON/OFF resistance ratio over ~10^4, and a medium set voltage of ~4 V. Further increasing the gelatin thickness leads to decrease in ON/OFF resistance ratio, possibly due to easy breakdown of the conductive filaments in the film. It is clear that the 80 nm is the optimal thickness of the gelatin dielectric layer for the memristors.

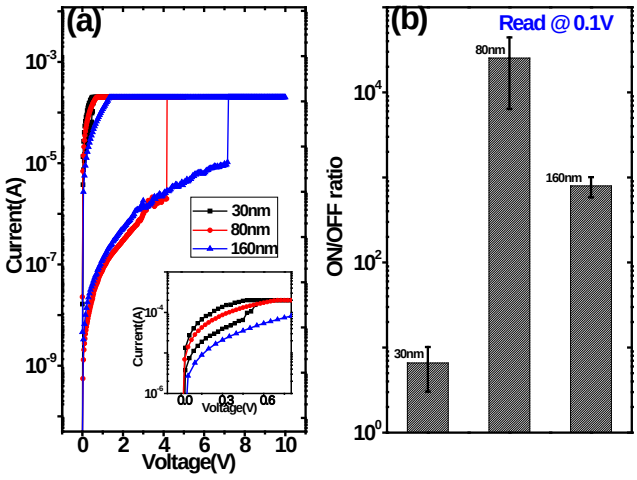

Figure 5. (a) I-V curves for the devices with different gelatin film thickness, and (b) ON/OFF resistance ratio of the memristors at 0.1 V bias. The inset is the I-V curves from the 30 nm gelatin layer device in details. The device with 80 nm gelatin film showed the best performance with the highest HRS/LRS

resistance ratio. The error bars are results from three arrays of devices measured.

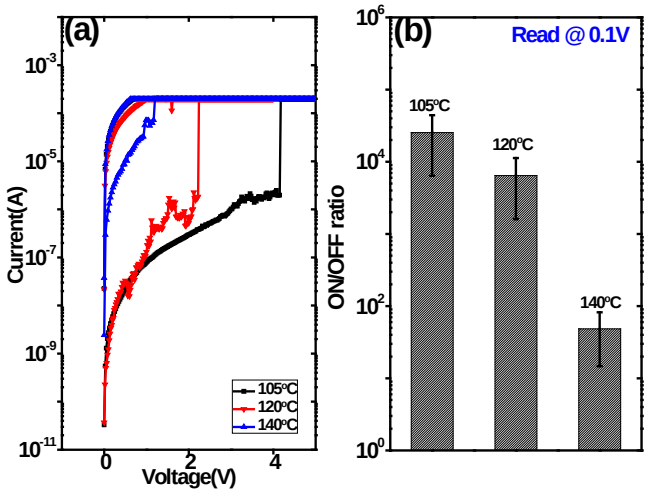

Figure 6. (a) Comparison of I-V curves for gelatin memristors with different baking temperatures, and (b) ON/OFF resistance ratio of gelatin memristors at 0.1 V bias. The error bars are results from three arrays of devices measured.

The baking temperature for the gelatin film was also found to have a profound effect on the switching behavior of the memristors. Fig. 6(a) shows the dependence of the I-V curves for the devices with the gelatin films baked at 105, 120 and 140 ^{o}C, respectively, with the gelatin film thickness fixed at 80 nm. The sandwich devices do not show any resistive switching behavior when the baking temperature is lower than 80 ^{o}C. The device is conductive and can't be formed. It is believed that there exist high concentration of mobile ions and residual water in the gelatin film. The mobility of the ions mediated by water leads to "high conductivity" of the film when it is not polymerized properly, unable to obtain a resistive switching behavior. However, when the baking temperature increases to 105, 120,140 ^{o}C respectively, the set voltage of the devices decreases from 4.5, 2.5 and 1.05 V correspondingly. When the baking temperature is 140 ^{o}C or higher, the devices would break down easily at high voltage without forming a resistive switching behavior. This may be due to the stronger fixation of ions and elements in the film which requires higher electric field for ions and elements to move, and the slow oxidation and reduction process at drier condition. Fig. 6(b) is the ON/OFF resistance ratio of the devices with different baking temperatures. Three arrays of devices were measured for each group the variation of the results is expressed by the error bars in the figures. Although the ON/OFF resistance ratio varies from sample to sample, the overall ON/OFF resistance ratios for the devices with a baking temperature

of 105 ^{o}C and 120 ^{o}C are about or over 10^4, much higher than those with a baking temperature of 140 ^{o}C which has much lower HRS resistances.

C. Switching mechanism

The filamentary model is the most common one used to explain the resistive switching behaviors of memristors, especially those with oxide dielectric layers [14,22,25]. Oxidation and reduction of metallic elements in the conductive filaments once formed is responsible for the OFF and ON states of the devices. Hopping conduction in dielectric is another possible mechanism for the resistive switching devices, but mostly for polymer-based memristors[23].

Our devices showed a perfect Ohmic behavior at the LRS, indicating they are probably dominated by conductive filaments in the gelatin dielectric layer at the LRS. C-AFM measurement was then conducted to clarify the switching mechanism of the memristor devices (80 nm gelatin thickness, 105 ^{o}C baking temperature). The device does not have the top electrode, and the C-AFM Pt-coated Si tip was used as an acting top electrode to induce the device into the LRS by applying a voltage to the AFM tip during its scanning. Figs. 7(a) and (b) show the conductive AFM images of the gelatin film with a positive voltage of 2.0 and 4.5 V applied, respectively, to the AFM tip. The AFM scanning area is 2 μm x 2 μm for both the tests. At a bias of 2.0 V, there is no electric current flowing between the AFM tip and the bottom electrode, i.e. no conductive path is formed in the gelatin film, and the gelatin film is an insulator. With further increasing the voltage applied to the AFM tip, tiny discrete conductive paths (filaments) are formed across the film, i.e. locally the gelatin film is turned to be conductive. The density of the tiny conductive filaments increases with the increase of bias, and at 4.5 V, which is above the set voltage used for the device with an identical gelatin layer, a high density of conductive filaments is formed as shown in Fig. 7(b). Such a high density of conductive filaments for an active area of 100 μm × 100 μm would be sufficient to conduct high “set” currents as shown in Figs. 3, 5 and 6, and the device would change from the OFF state to ON state. The C-AFM results have clearly demonstrated that the conductive filaments are responsible for the switching behavior of the memristors fabricated.

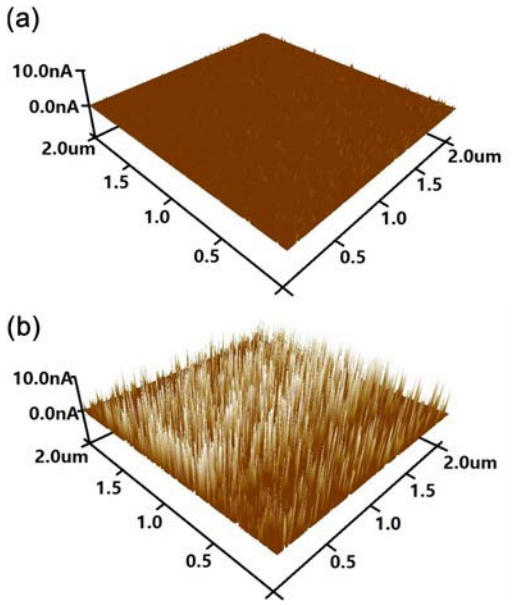

Figure 7. (a) and (b) are the HRS and LRS version of the C-AFM images. (b) shows that there is a high density of metallic filaments in the gelatin film when a bias of 4.5 V is applied to the tip of the C-AFM for the measurement, which corresponds to the set voltage of the device with identical gelatin layer.

Metals such as Mg and W used in this work are easy to dissolve in water [13], hence their ions and elements can diffuse into the gelatin film easily, and may be responsible for the conductive filaments in the gelatin film under high electric field. However, we have made gelatin memristors with various metal electrodes, Mg, Al, Au, Ag, W with work function varying from 3.6 to 5.5 eV and most of them are almost insoluble. These devices all show resistive switching behavior though the set and reset voltages are different from each other slightly. Similar results were also reported by Chang et al with various metal electrodes[19]. Both the results indicate that the type of metals only affect the set/reset voltage values, but not the switching behavior of the gelatin memristors, and the resistive switching behavior is, therefore, correlated mainly to gelatin material itself.

It is well known that gelatin contains a high density of mobile ions such as Fe^{+3}, Al^{+3}, Mg^{+2}, K^{+}, Na^{+} etc. We believe these mobile ions, particularly Fe^{+3}, Al^{+3}, Mg^{+2} ions, are responsible for the formation of conductive filaments and the resistive switching behavior observed [26]. Under the initial forming process, mobile ions move along the electric field, particularly those localized areas with strong electric field, and connect the top electrode with the bottom one. Once reached the bottom electrode, they stop move further due to screening effect. Meanwhile electrons are also injected simultaneously from the bottom electrode under a positive bias, and reduce the ions to

metallic elements, forming conductive filaments and leading to dramatic reduction of the resistance, i.e. the LRS. The general reaction for these reactive metal ions is

$$M^{+x} + xe^{-} \leftrightarrow M \quad (1)$$

here M represents reactive metal elements such as Fe, Mg, x is an integral number with a typical value of 2 or 3 for transitional metals and e^{-} the electron charge. During the reset process with a negative bias applied to the top electrode, metal elements in the gelatin layer are easily oxidized with the reaction process from the right side to left side of equation (1) due to the easy oxidation nature of transitional metal elements, leading to rupture of the conductive filaments. Metal elements near the top electrode lose the electrons easiest, thus oxidation of elements occurs mostly near the top electrode. Once the filaments are broken, the remaining metallic elements will stay in the places, making the dielectric gap between the top electrode and remaining filament shorter than the distance between the two electrodes. This is why the set voltage is always smaller than the forming voltage for a memristor. The set process is similar to that of forming process with smaller set voltage.

W and Mg metals are used as the bottom and top electrodes respectively, they are elements easily dissolving into water (become oxidized) as demonstrated by our previous work with Albumen dielectric film [15]. Gelatin solution was spun on W electrodes, therefore some of W elements will diffuse into the gelatin and are oxidized. Mg is much easier to be dissolved into water than W, even though Mg was deposited on a baked gelatin film, a certain amount of Mg elements is expected to diffuse into the gelatin film after the device fabrication. Therefore, we believe both W and Mg elements in the gelatin film contribute a great deal to the formation of conductive filaments observed by the C-AFM measurement. More work is needed to clarify this.

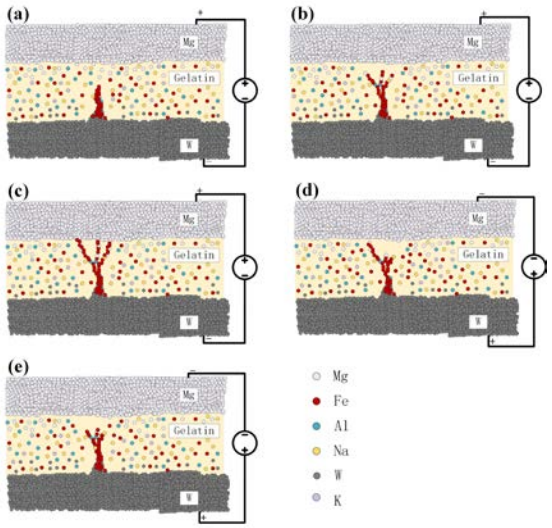

Figure 8. (a~c) show the forming process of the conductive filament in the gelatin layer under a positive bias, and (d~e) the break progress of the conductive filaments under reverse bias.

Based on the results obtained and above discussion, we propose a mechanistic model to explain the resistive switching behavior as shown in Fig. 8. For the set process, electrons are injected from the bottom electron, gradually filling up the space charges and reducing ions into metal elements as is shown in Fig. 8(a), corresponding to process (1) with a slope of ~1.3 (Fig. 3b). With further increase in bias, the injected electrons are transported ballistically through the dielectric film as shown in Fig. 8(b), corresponding to the Mott−Gurney law with a slope of ~2-3 as shown in Fig. 3b for process step (2). Once all the reactive ions are reduced, the device is at the LRS (Fig. 8(c)), dominated by an ideal Ohmic conduction with a slope of 1.02 for process (3). For Reset process, a negative voltage is applied to the device, and it is an Ohmic conduction until the filaments are broken (Fig. 8(d)), hence the slope of the I-V curve approaches the unity as represented by process (4) in Fig. 3b. Fig. 8(e) shows that the device returns to the initial HRS, and is dominated by process (5) and (6) in Fig. 3b.

IV. CONCLUSIONS

In summary, the crossbar Mg/gelatin/W memristors have been fabricated and characterized. The influence of gelatin layer thickness and baking temperature on device performance has been investigated. The optimal devices showed that the HRS/LRS resistance ratio is over 10^2, and the

performance of the device remains stable for a duration over 10^6 sec with the constant resistances for the HRS and LRS, demonstrating its high stability. Conductive AFM measurements revealed a high density of tiny conductive filaments in the gelatin film after applying a bias of 4.5 V (corresponding to the set voltage), provided a direct evidence for the conductive filament model of the resistive switching devices.

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